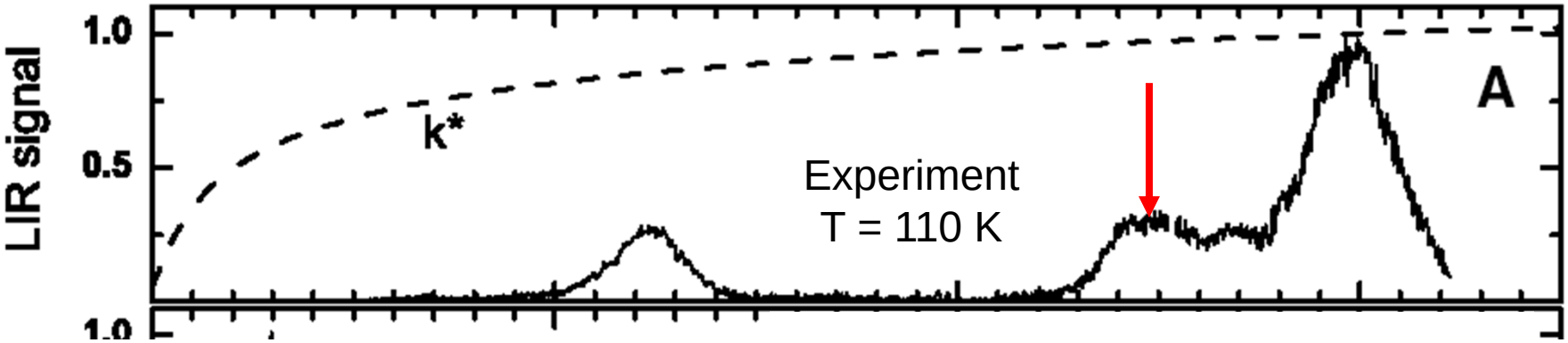
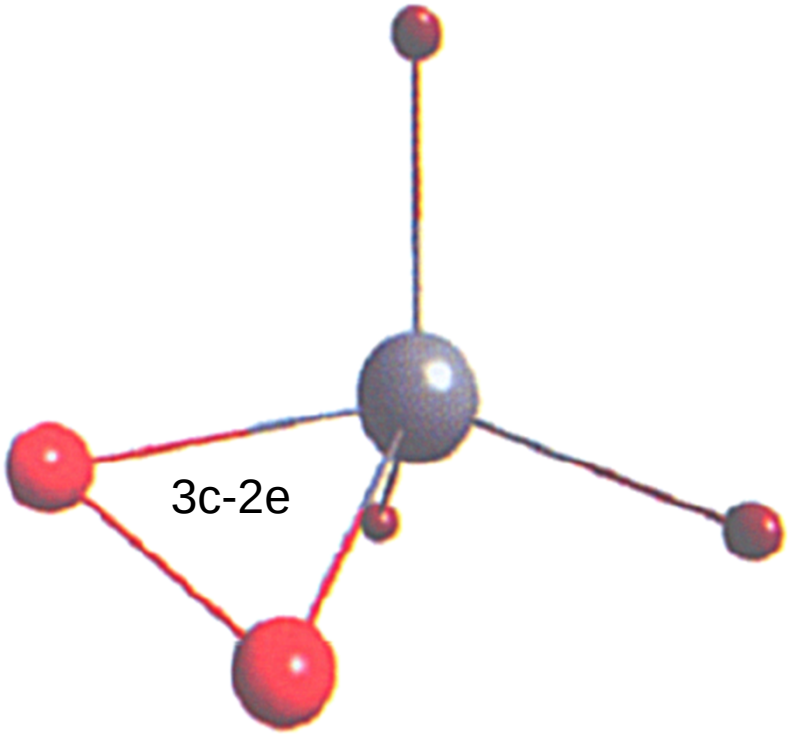
IR SPECTRA OF COLD PROTONATED METHANE

O. Asvany, **K. Yamada**, S. Brünken, A. Potapov & S. Schlemmer
I. Physikalisches Institut, Universität zu Köln, Germany

CH_5^+: LIR Spectrum and *Ab Initio* Simulations

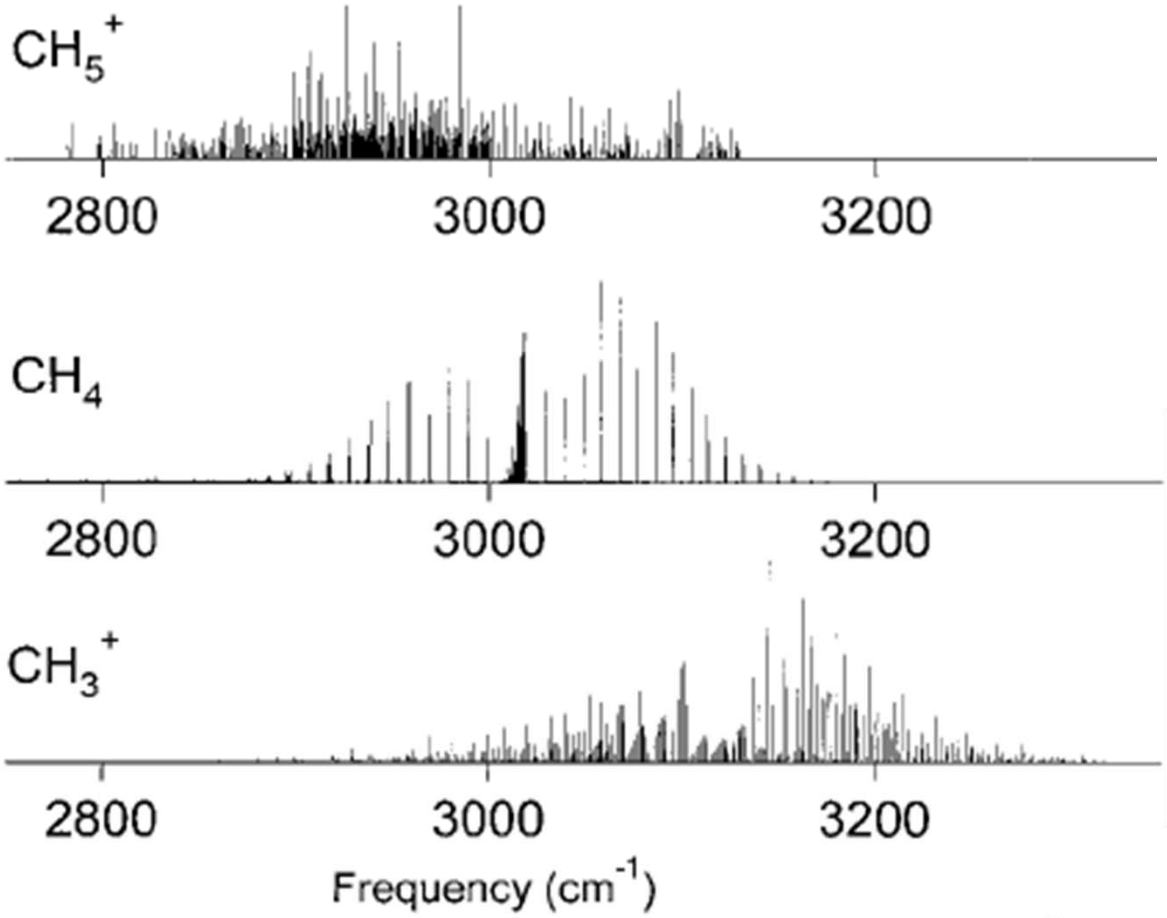




Asvany et al., Science, 309 (2005)

CH_5^+: The Infrared Spectrum Observed

E. White, J. Tang & T. Oka, SCIENCE, vol. 284 (**1999**) 135



1000 lines, no assignment

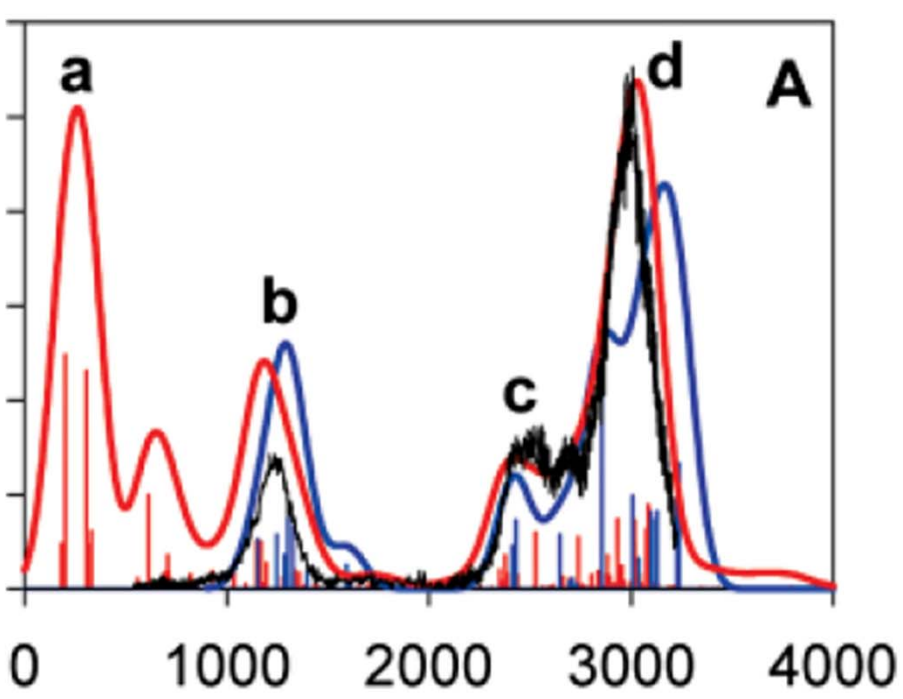
„Experimentally the next step will be to observe the spectrum at low temperatures and to observe deuterated species“

CH_5^+: The Cheshire Cat Smiles

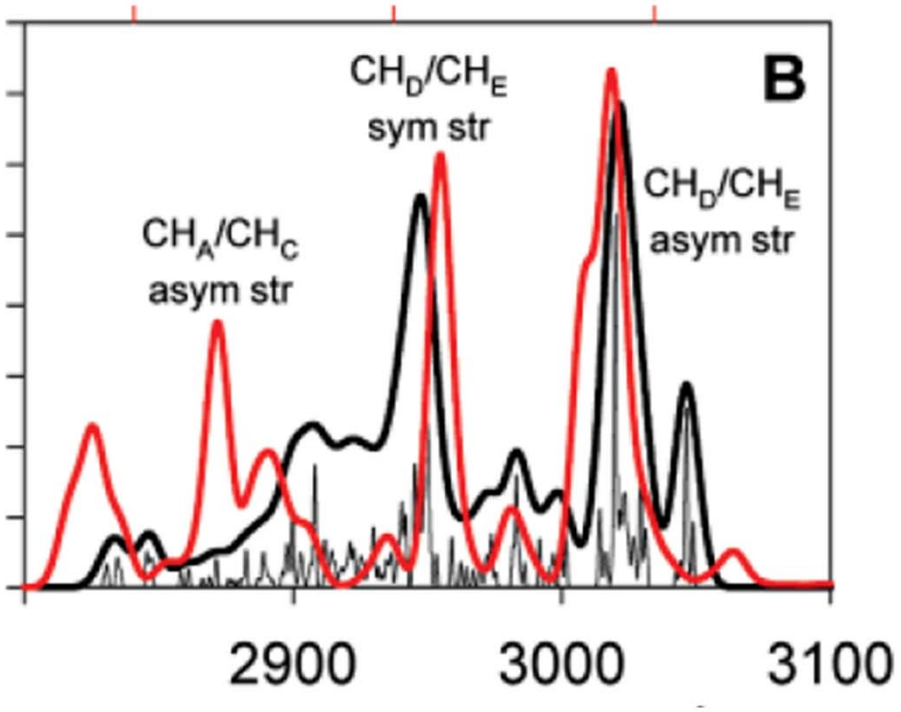
Marx & Parinello, SCIENCE, vol. 284 (**1999**) 59

Quantum Deconstruction of the Infrared Spectrum of CH_5^+

X. Huang, A. McCoy, J. Bowman, L. Johnson, C. Savage, F. Dong, D. Nesbitt,
SCIENCE, vol. 311 (**2006**) 60



Frequency cm^{-1}

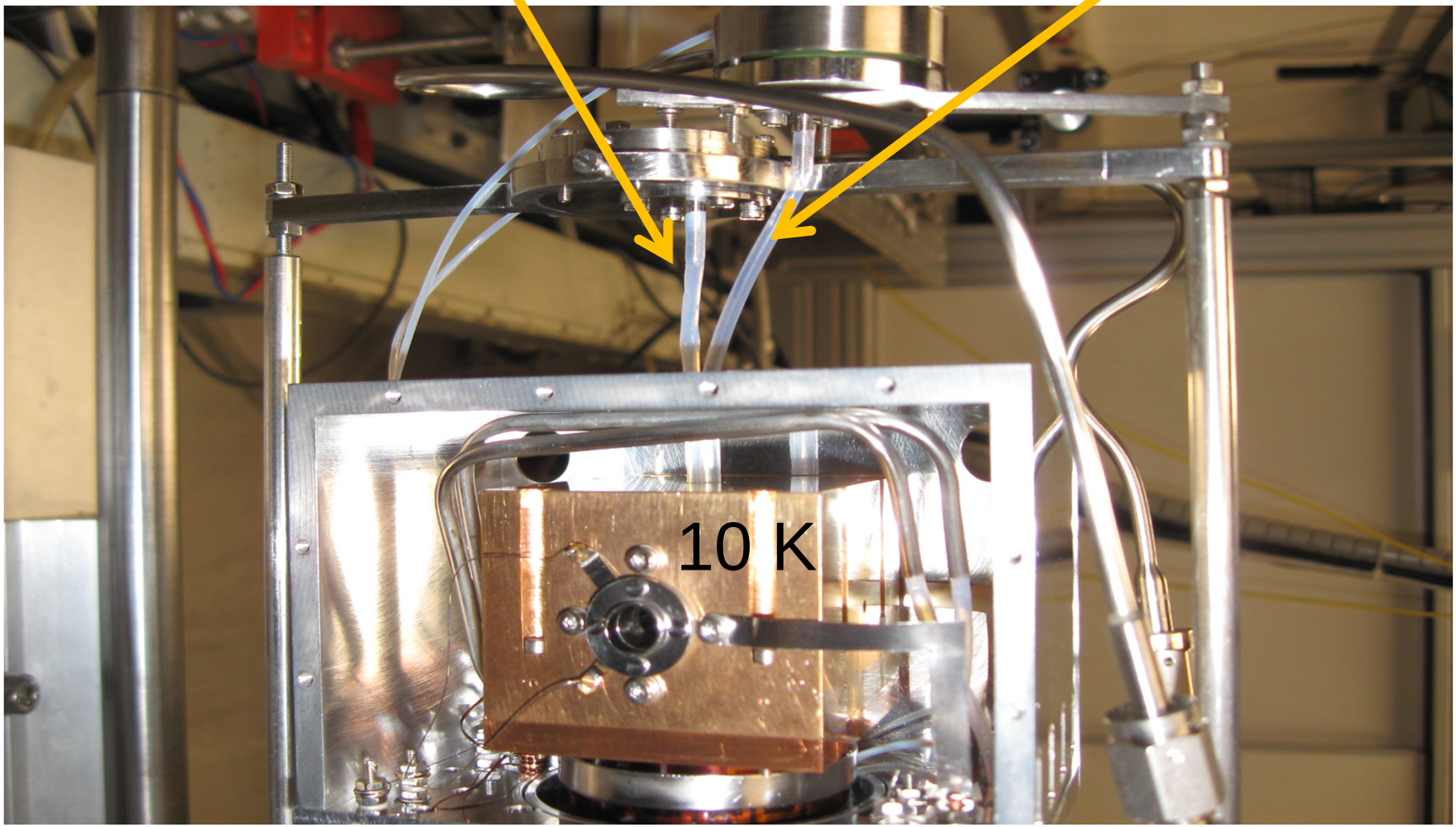


Frequency cm^{-1}

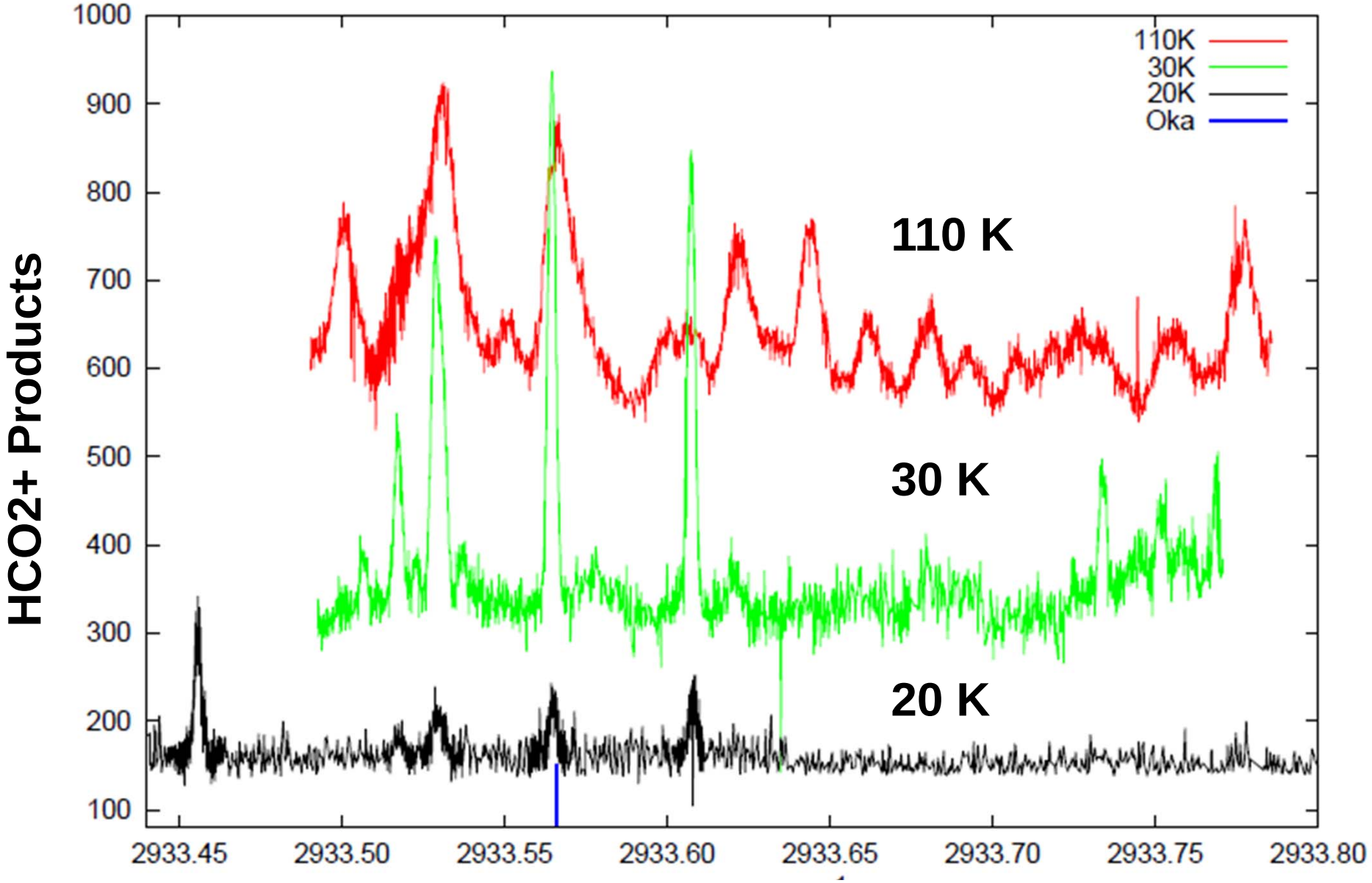
Low Temperature & High-Resolution?

Cooling: He

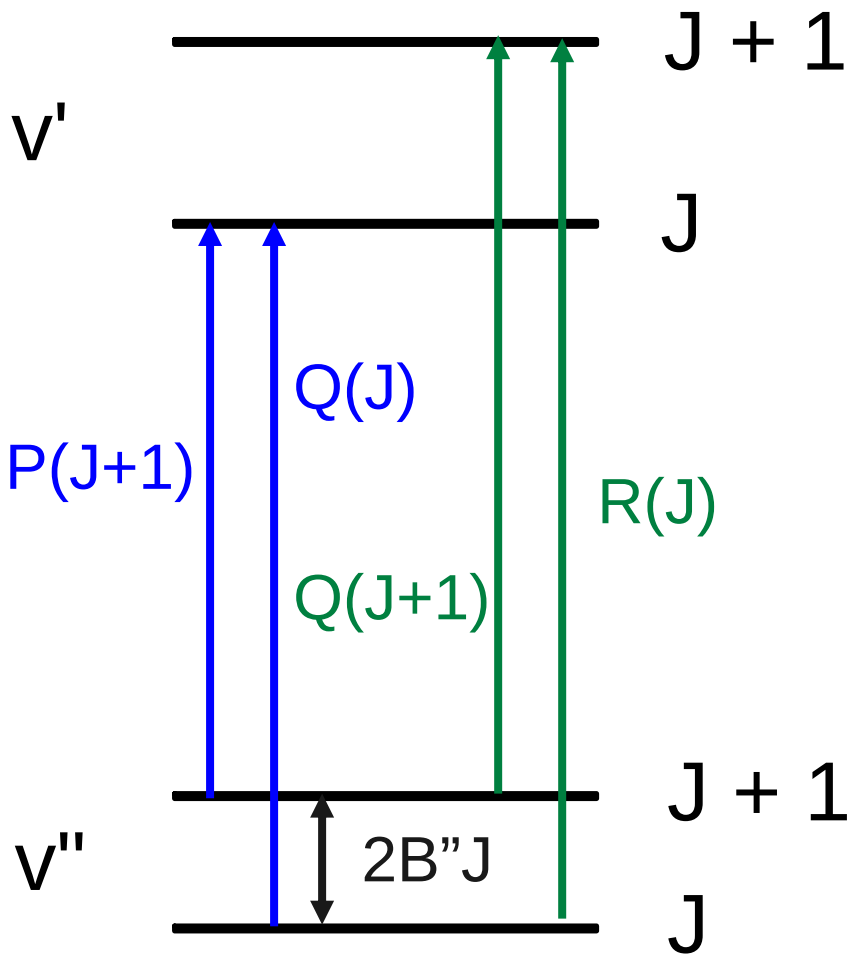
Reaction: CO_2



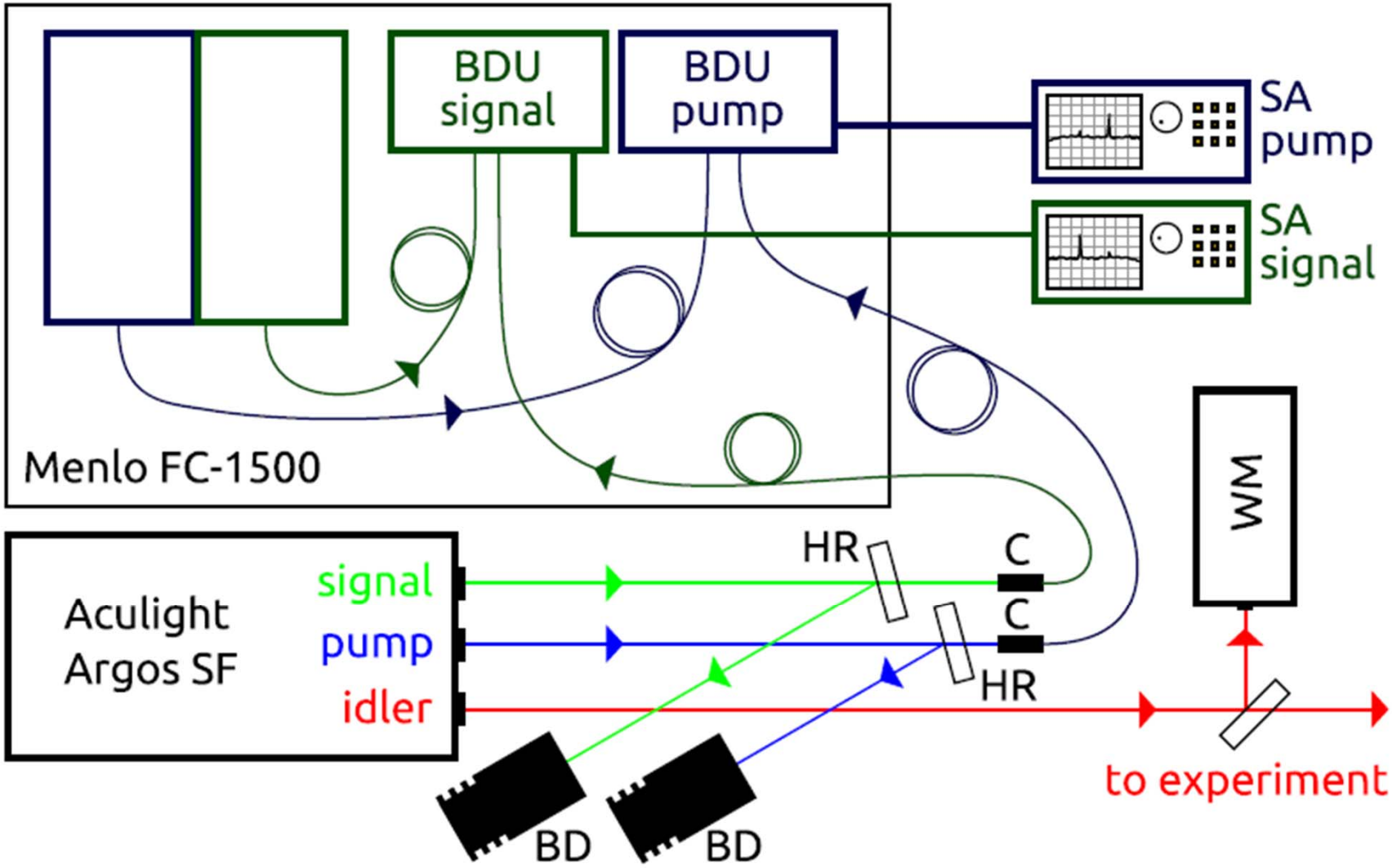
Low Temperature, High-Resolution Spectra !



Rotational Structure of IR Spectra
Four Line Combination Differences (4LCD)

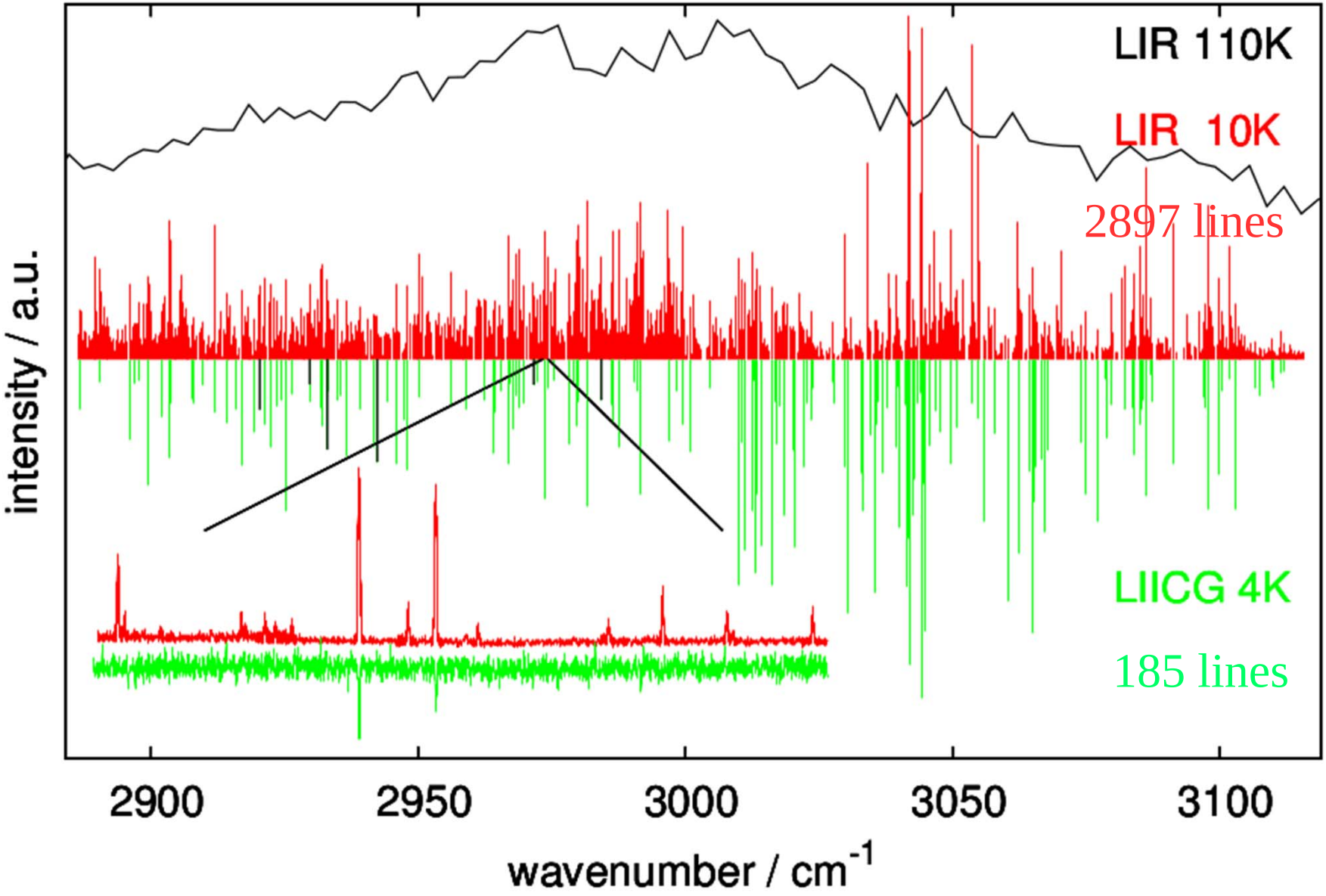


Calibration: Wavemeter & Frequency Comb



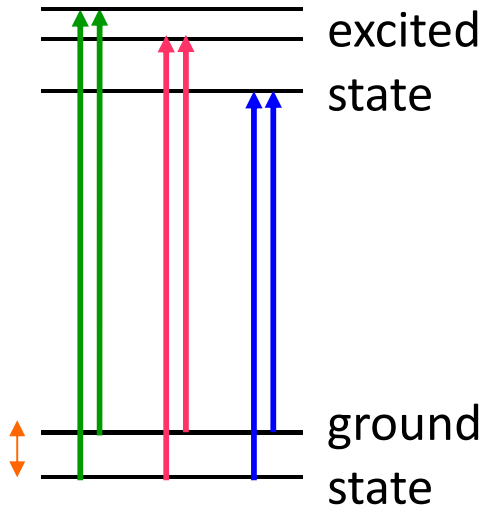
$$h\,\nu_{idler} = h\,\nu_{pump} - h\,\nu_{signal}$$

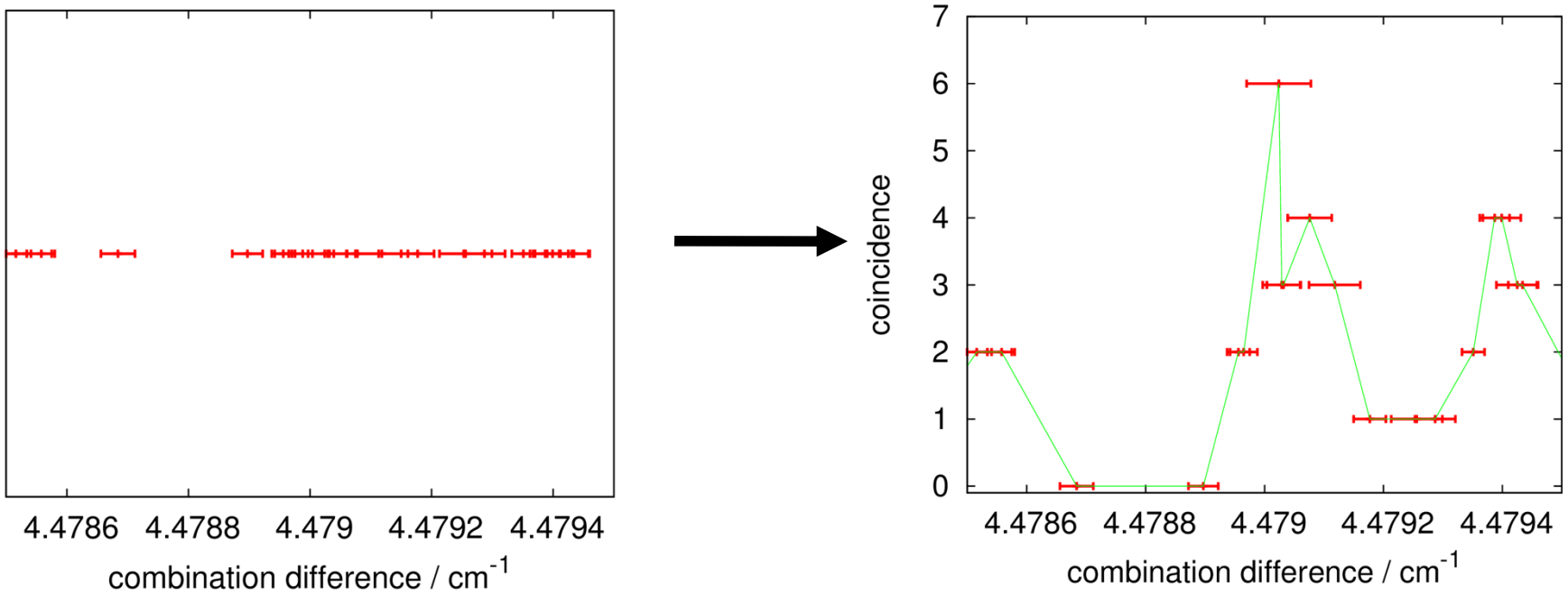
Results: Highly Accurate Linelist



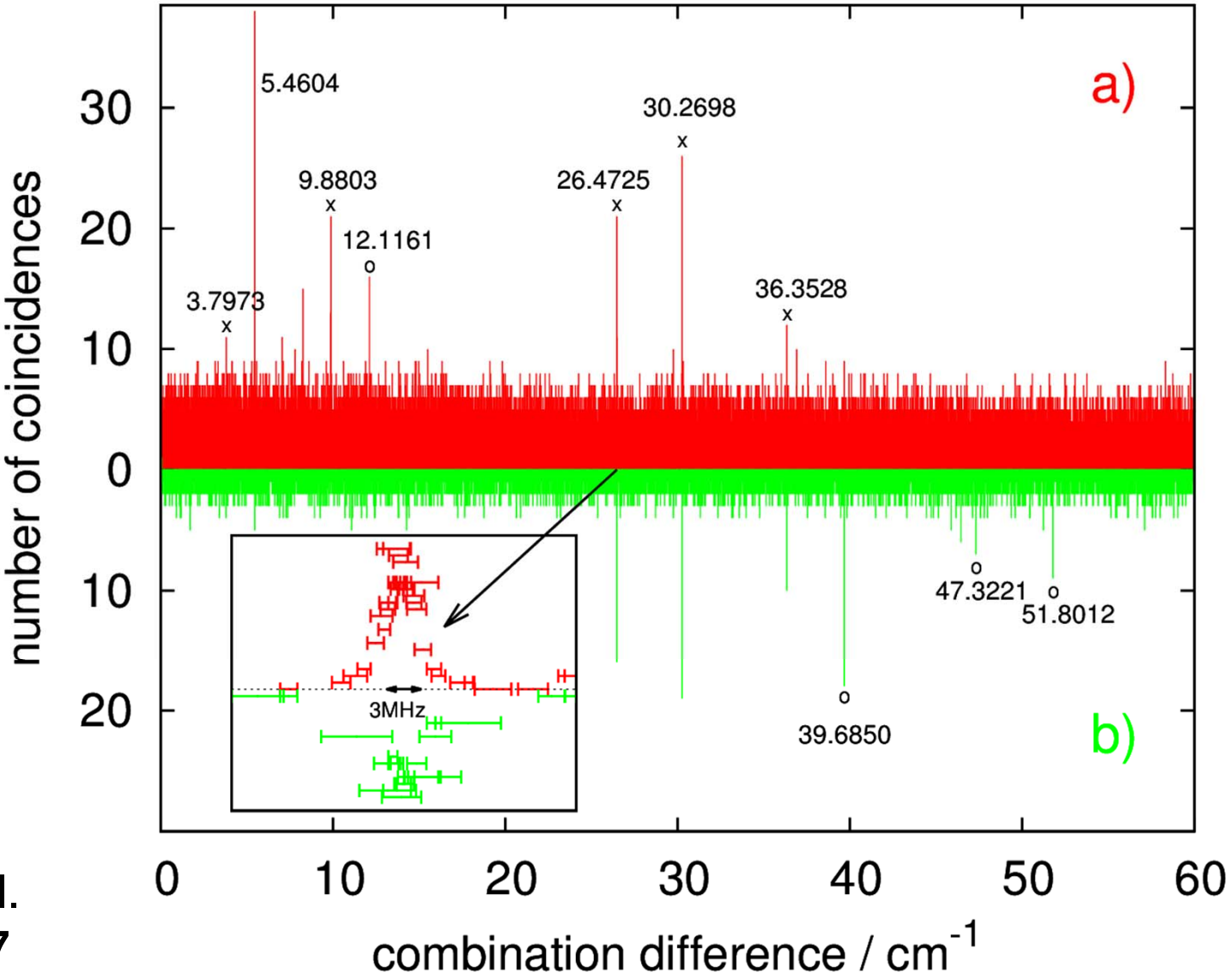
Combination Differences

N measured lines:
N/2 (N-1) unbiased combination differences





Combination Difference Spectrum



Asvany et al.
Science **347**
1346 (2015)

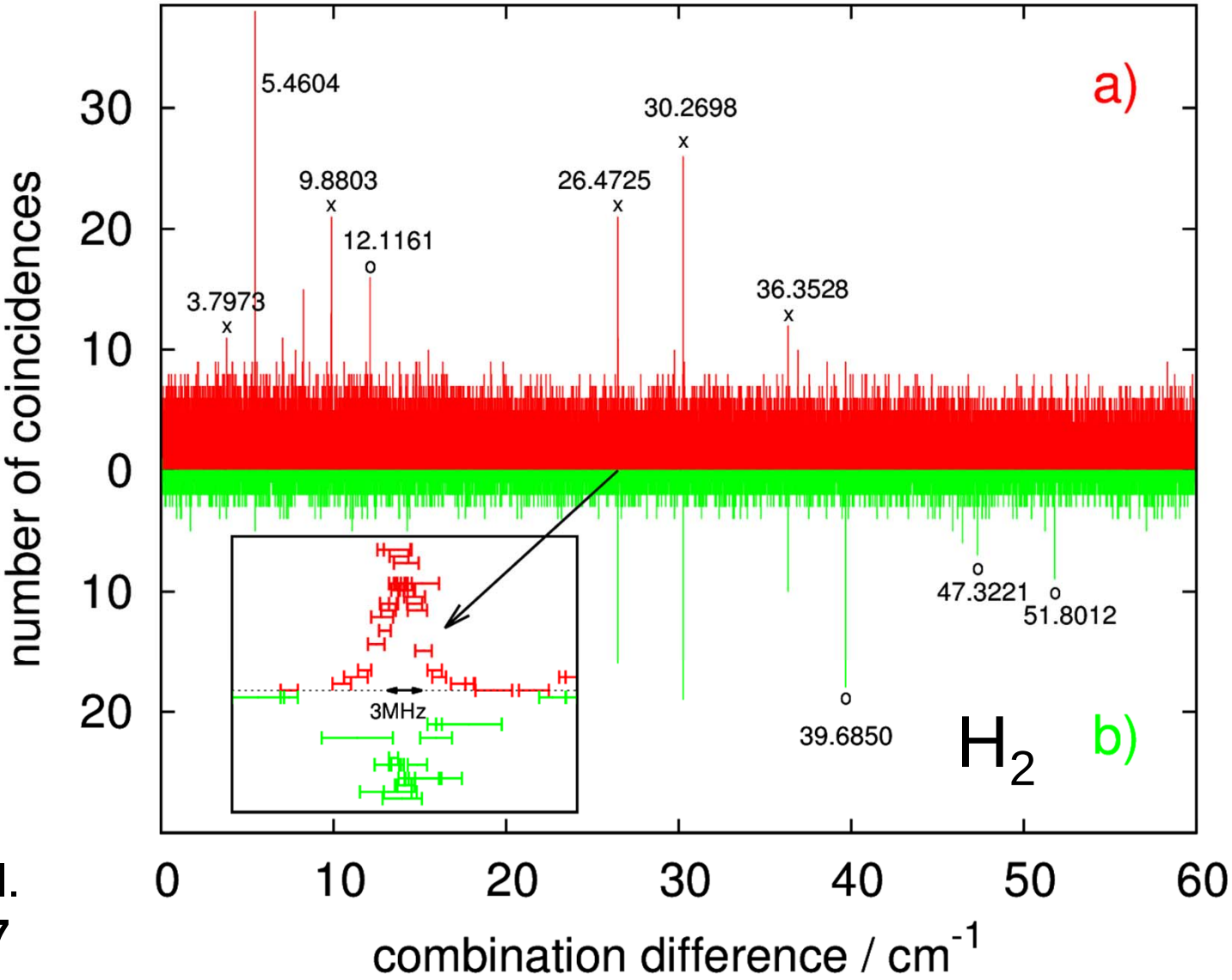
Reconstruction of lowest energy levels

Intensities of spectral lines:

statistical weights

A_2	G_2	H_2
I=5/2	3/2	1/2
6	4	2
		weak

Combination Difference Spectrum



Asvany et al.
Science **347**
1346 (2015)

Reconstruction of lowest energy levels

Intensities of spectral lines: statistical weights

A_2	G_2	H_2
I=5/2	3/2	1/2
6	4	2
		weak

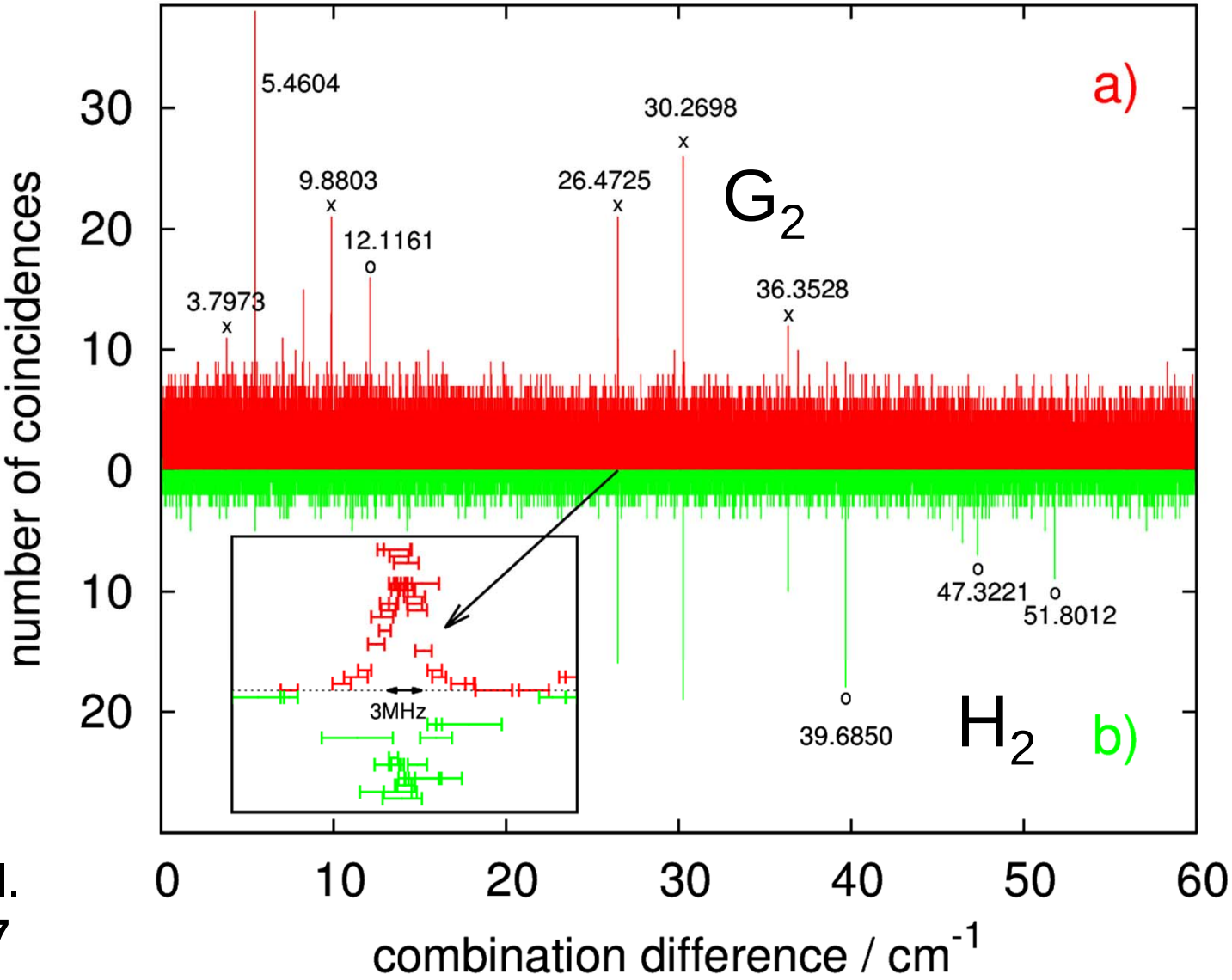
Number of states

A_2	G_2	H_2
1	4	5

# of CDs

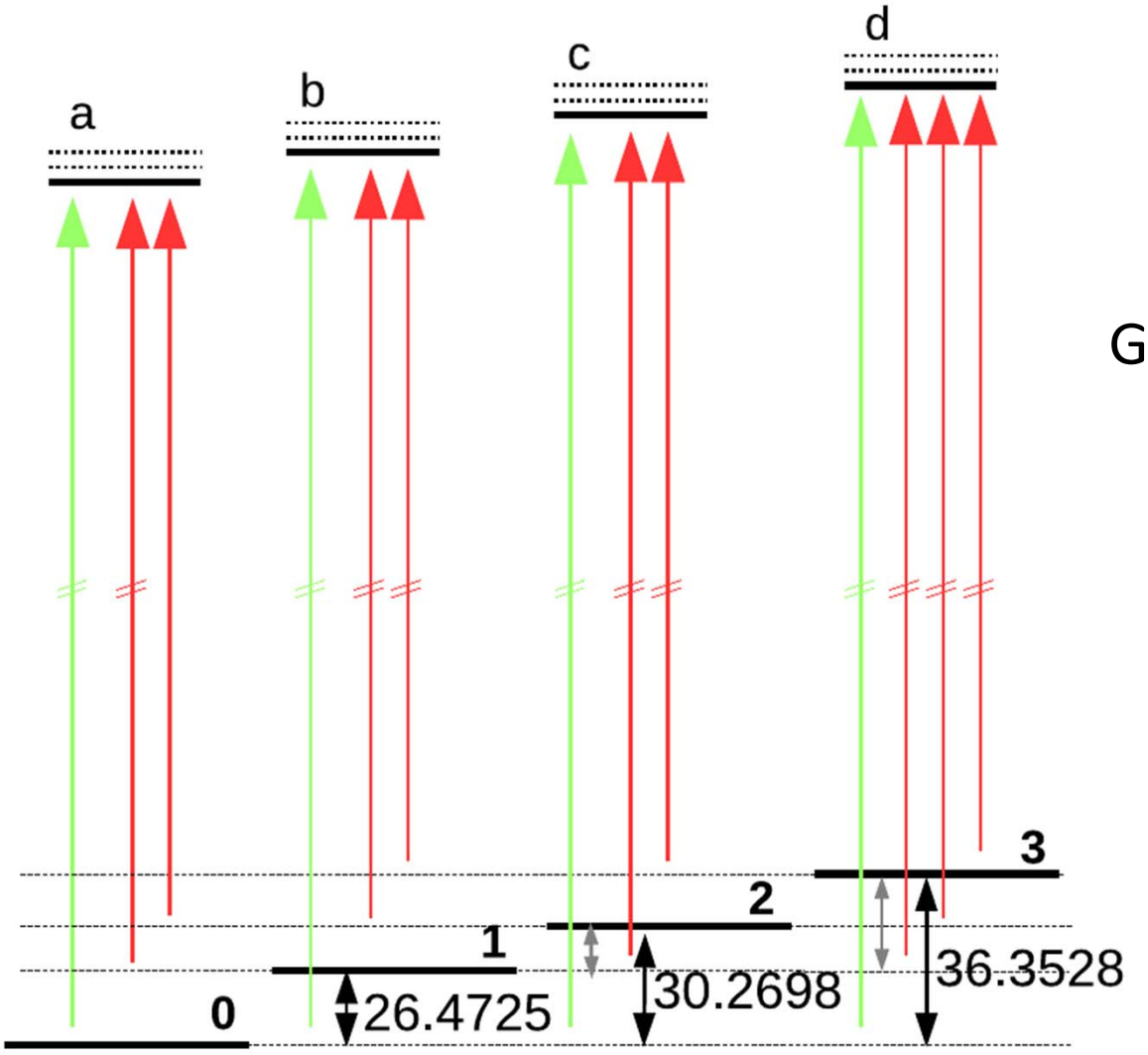
A_2	G_2	H_2
1	16	25
weak		

Combination Difference Spectrum



Asvany et al.
Science **347**
1346 (2015)

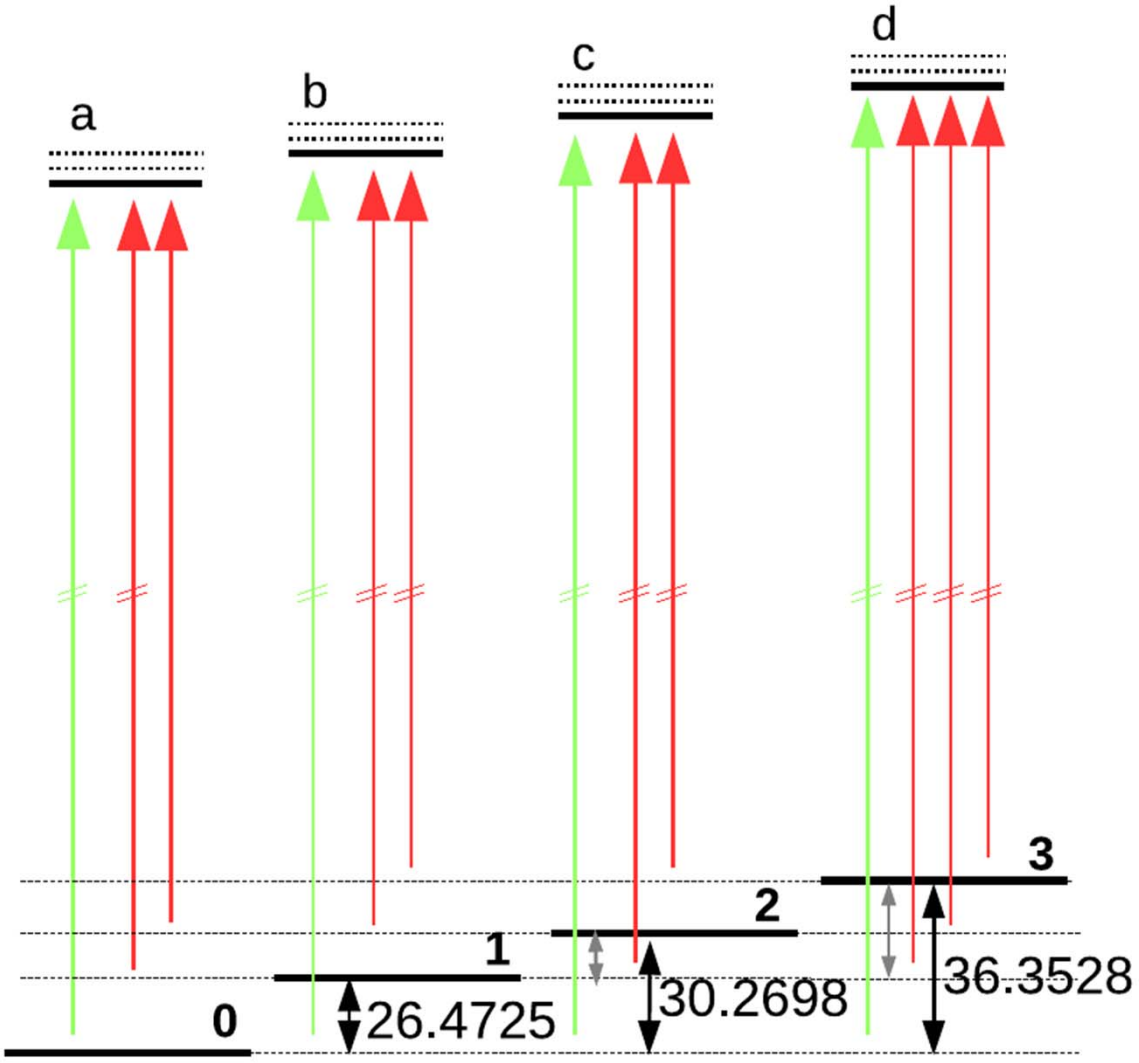
Reconstruction of lowest energy levels



Ground state energy level scheme

G_2 species

Reconstruction of lowest energy levels



G_2 states:

Level	J”
0	0
1	2

$\Delta E \sim 6\ B$

$B \sim 4\ cm^{-1}$

IR SPECTRA OF COLD PROTONATED METHANE

- Lowest energy terms: A_2 G_2 H_2

Next Steps

- Coupling of *vibration* and *rotation*
- Model Hamiltonian ?
- THz spectrum ?
- $CH_nD_{5-n}^+$
- Solvation: $CH_5^+(H_2)_n$
- ….